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(54) Well drilling and servicing fluids and removal of filter cake deposited thereby

(57) Well drilling and servicing fluids for use in producing formations comprise water, a water-soluble salt and a particulate solid bridging agent selected from magnesium oxychloride cement, magnesium oxysulfate cement, magnesium potassium phosphate hexahydrate, magnesium hydrogen phosphate trihydrate and magnesium ammonium phosphate hexahydrate. The filter cake so deposited is removed by contact with an aqueous clean-up solution containing an organic acid, a hydrolyzable ester, an ammonium salt, a chelating agent or a mixture of an ammonium salt and a chelating agent.

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ammonium phosphate hexahydrate. As mentioned, the bridging agent can include weighting materials and/or certain filler materials. The drilling and servicing fluid, the bridging agent therein or the aqueous clean-up solution can also include an oxidizer or other breaker which breaks up polymer in the filter cake.

[0012] In the well drilling and servicing fluids of this invention, the particulate solid bridging agent is a synthesized inorganic compound of the type generally referred to as a chemically bonded ceramic. The particulate solid bridging agent is soluble in an aqueous clean-up solution containing a mild organic acid, a hydrolyzable ester, an ammonium salt, a chelating agent or a mixture of an ammonium salt and a chelating agent. When required, a fluid loss control agent and/or a hydratable polymer solids suspending agent can optionally be included in the well drilling and servicing fluids.

[0013] The water soluble salt in the drilling and servicing fluids of this invention can be one or more of sodium chloride, sodium bromide, sodium acetate, sodium formate, sodium citrate, potassium chloride, potassium formate, cesium formate, calcium chloride, calcium bromide and mixtures thereof. Common oilfield brines can be utilized in the drilling and servicing fluids in place of water and a water soluble salt. Oilfield brines are often preferred due to their ready availability in the oilfield.

[0014] A variety of fluid loss control agents can be utilized in the well drilling or servicing fluids, including, but not limited to, starch, starch ether derivatives, hydroxyethylcellulose, cross-linked hydroxyethylcellulose and mixtures thereof. Of these, starch is the most preferred. When used, the fluid loss control agent is generally included in the salt solution or brine in an amount in the range of from about 0.1% to about 2% by weight of the salt solution or brine, more preferably in the range of from about 1% to about 1.3% and most preferably about 1.3%.

[0015] A variety of hydratable polymer solid suspending agents can also be utilized, including, but not limited to, biopolymers such as xanthan and succinoglycon, cellulose derivatives such as hydroxyethylcellulose and guar and its derivatives such as hydroxypropyl guar. Of these, xanthan is preferred. When used, the hydratable polymer is generally included in the drilling or servicing fluid in an amount in the range of from about 0.1% to about 0.6% by weight of the salt solution or brine, more preferably in the range of from about 0.13% to about 0.16% and most preferably about 0.13%.

[0016] In accordance with this invention, the particulate solid bridging agents are synthesized inorganic compounds of the type generally referred to as chemically bounded ceramics that are substantially insoluble in water, but are substantially soluble in the aqueous clean-up solution used. Examples of such chemically bounded ceramics include, but are not limited to, magnesium oxychloride cement, magnesium oxysulfate cement, magnesium hydrogen phosphate trihydrate, magnesium potassium phosphate hexahydrate and magnesium ammonium phosphate hexahydrate.

[0017] Magnesium oxychloride cement is prepared by mixing magnesium oxide, magnesium chloride and water. Magnesium oxysulfate is prepared by mixing magnesium oxide, magnesium sulfate and water. Magnesium hydrogen phosphate trihydrate is prepared by mixing magnesium oxide, phosphoric acid and water. Magnesium potassium phosphate hexahydrate is prepared by mixing magnesium oxide, monopotassium phosphate and water. Magnesium ammonium phosphate is prepared by mixing magnesium oxide, monoammonium phosphate and water.

[0018] Other materials can be added to the ceramic compounds described above to achieve desired results or properties. For example, particulate weighting materials such as barite, iron oxide and manganese oxide can be included therein. As mentioned above, oxidizers and other polymer breakers can also be included. Many other useful additives will suggest themselves to those skilled in the art.

[0019] The bridging agent utilized in the drilling or servicing fluid is generally included therein in the amount of from about 5% to about 60% by weight of the aqueous salt solution or brine, more preferably in the range of from about 10% to about 27% and most preferably about 14%.

[0020] As will be understood by those skilled in the art, the particulate solid bridging agent is deposited by the drilling or servicing fluid on the walls of the well bore in the producing zone being drilled or serviced along with other solid particles and gelled fluid loss control polymers, suspending agent polymers and the like. Upon completion of the drilling or servicing operation, an aqueous clean-up solution containing a mild organic acid, a hydrolyzable ester, an ammonium salt, a chelating agent or a mixture of an ammonium salt and a chelating agent is introduced into the well bore whereby the particulate solid bridging agent in the filter cake is dissolved.

[0021] The well drilling and servicing fluid or the bridging agent therein or the clean-up solution can contain an oxidizer or other breaker which functions to oxidize and break up gelled polymeric fluid loss control additives, suspending agents and the like in the filter cake. The breaking up of the polymeric materials allows the particulate solid bridging agent to be dissolved by the clean-up solution in a shorter period of time. Generally, any oxidizer or other breaker that can be deposited with the filter cake and is substantially inactive until contacted with an aqueous clean-up solution can be utilized in the well drilling and servicing fluid or in the bridging agent. For example, oxidizers that are substantially insoluble in water but are soluble in the clean-up solution can be utilized. Oxidizers or other breakers that can be encapsulated with a material that is insoluble in water but soluble in the clean-up solution or that can be encapsulated in the bridging agent can also be used.

[0022] Various oxidizers and breakers that can be incorporated into the particulate solid bridging agent when it is

the bridging agent particles out of the presence of an ammonium salt or salts. The chelating agent can be included in the drilling or servicing fluid and the ammonium salt utilized can be delivered in encapsulated form or generated in-situ. Various other techniques known to those skilled in the art for providing delays can also be utilized such as delivering the chelating agent as an ester that slowly hydrolyzes to the acid chelating form, utilizing a chelating agent that is not effective at a particular pH and introducing a second agent to change the pH to a level where the chelating solution dissolves bridging particles, and other similar variations.

[0034] In accordance with the methods of this invention, filter cake is removed from the walls of a well bore penetrating a producing formation. The filter cake is deposited in the well bore by a drilling or servicing fluid of this invention basically comprised of water, a water soluble salt and a particulate solid bridging agent. The methods are basically comprised of the following steps. The particulate solid bridging agent utilized in the drilling or servicing fluid is a synthetic inorganic compound which dissolves in an aqueous clean-up solution containing a mild organic acid, a hydrolyzable ester, an ammonium salt, a chelating agent, or a mixture of an ammonium salt and a chelating agent. After the drilling or servicing fluid is removed from the well bore, the filter cake remaining on the walls of the well bore including the bridging agent is contacted with the clean-up solution used for a period of time such that the bridging agent is dissolved thereby. As mentioned above, the drilling or servicing fluid can include a fluid loss control agent and a polymeric solids suspension agent. As also mentioned above, the drilling or servicing fluid, the bridging agent therein or the aqueous clean-up solution can include an oxidizer or other breaker which oxidizes and breaks up gelled polymer in the filter cake. Also, as mentioned above, after the clean-up solution breaks up gelled polymer in the filter cake and dissolves the bridging agent therein, a wash solution can be utilized to remove the remaining filter cake from the walls of the well bore or the remaining filter cake can be removed by producing the formation.

[0035] A particularly suitable method of this invention for removing filter cake from the walls of a well bore penetrating a producing formation deposited therein by a drilling or servicing fluid is comprised of the following steps. A drilling or servicing fluid is utilized comprised of water, a water soluble salt selected from the group consisting of sodium chloride, sodium bromide, sodium acetate, sodium formate, sodium citrate, potassium chloride, potassium formate, cesium formate, calcium chloride, calcium bromide and mixtures thereof or one or more brines containing such salts, a fluid loss control agent comprised of starch, a xanthan polymer solids suspending agent and a particulate solid chemically bonded ceramic bridging agent selected from magnesium oxychloride cement, magnesium oxysulfate cement, magnesium potassium phosphate hexahydrate, magnesium hydrogen phosphate trihydrate or magnesium ammonium phosphate hexahydrate, and a particulate solid magnesium peroxide oxidizing agent which is activated by contact with an ammonium salt to oxidize and break up gelled polymer in the filter cake. Thereafter, the filter cake produced by the drilling or servicing fluid is contacted with an aqueous clean-up solution containing ammonium chloride, a chelating agent or ammonium chloride and a chelating agent for a time period such that gelled polymer in the filter cake is oxidized and broken up by the magnesium peroxide and the bridging agent is dissolved by the clean-up solution. If required, a wash solution can next be utilized to contact the walls of the well bore and wash away any remaining filter cake thereon or the remaining filter cake can be removed by producing the formation. As mentioned above, various components of the drilling or servicing fluid and/or the cleaning solution can be delivered to the producing formation in encapsulated form or generated in-situ.

[0036] In order to further illustrate the drilling and servicing fluids and methods of this invention, the following examples are given.

Example 1

[0037] Horizontal wells are often completed utilizing servicing fluids which include particulate solid bridging agents that are deposited as a part of the filter cake on the walls of the well bores. The wells are completed by placing gravel packs in the producing zones and clean-up solutions are placed in the gravel packs and left to soak so that the filter cake is dissolved and removed. In a typical horizontal well completed with a gravel pack in an 8 ½" diameter well bore with 5 ½" diameter screens, the solubility of the bridging particles in the filter cake should be in the range of from about 0.5 to about 1.25 cubic centimeters of bridging particles per 100 cubic centimeters of clean-up solution. For bridging particles with specific gravities of greater than about 0.6, this means that about 1.5 to about 3 grams of bridging agent will be dissolved per 100 cubic centimeters of clean-up solution.

[0038] A procedure for testing clean-up solutions for dissolving various particulate bridging agent was developed as follows: 0.5 cubic centimeters of the particulate bridging agent tested are added to a 50 milliliter vial. The vial is then filled with clean-up solution, capped and placed in a 150° water bath for 24 hours. Thereafter, the solids in the vial are filtered using a preweighed filter. The filter with the solids thereon is dried and weighed to determine the weight of the undissolved solids. The solubility of the particulate bridging agent is then calculated in percent of solids dissolved.

[0039] Several bridging agents and clean-up solutions were tested using the above described procedure, and the results of the testing are given in Table I below.

TABLE III (continued)

Solubility Of Magnesium Potassium Phosphate In Additional Clean-Up Solutions				
Clean-Up Solution				
No.	Water, m/s	Ester	Chelating Agent	Observation
2	50	3 g dimethyl phthalate	4.4 g sodium citrate	Dissolved in 48 hrs
3	50	2.6 g dimethyl glutarate	4.4 g sodium citrate	Dissolved in 48 hrs
4	50	3 g DBE[1]	4.4 g sodium citrate	Dissolved in 72 hrs

[1]DBE (dibasic esters) is a mixture of dimethylglutarate, dimethyl succinate and dimethyl adipate.

[0043] From Table III, it can be seen that the clean-up solutions dissolved the magnesium potassium phosphate.

Claims

1. A well drilling or servicing fluid for use in producing formations to deposit filter cake therein, which fluid comprises water, a water-soluble salt and a particulate solid bridging agent, **characterised in that** said particulate solid bridging agent comprises a chemically bonded ceramic oxychloride cement, magnesium oxysulfide cement, magnesium potassium phosphate hexahydrate, magnesium hydrogen phosphate trihydrate or magnesium ammonium phosphate hexahydrate, which is dissolvable by an aqueous clean-up solution containing an organic acid, a hydrolyzable ester, an ammonium salt, a chelating agent or a mixture of an ammonium salt and a chelating agent.

2. A fluid according to claim 1, wherein said bridging agent includes a breaker encapsulated therein for breaking up polymer in said filter cake deposited by said fluid, said breaker preferably being activated by said clean-up solution.

3. A fluid according to claim 2, wherein said breaker is magnesium peroxide, magnesium peroxydiphosphate, strontium peroxide, barium peroxide, calcium peroxide, magnesium perborate, barium bromate, or any mixture of two or more thereof.

4. A fluid according to claim 1, 2 or 3, wherein said water-soluble salt is sodium chloride, sodium bromide, sodium acetate, sodium formate, sodium citrate, potassium chloride, potassium formate, cesium formate, calcium chloride, calcium bromide, or any mixture of two or more thereof.

5. A fluid according to claim 1, 2, 3 or 4, which further comprises a fluid loss control agent selected from starch, starch ether derivatives, hydroxyethylcellulose, cross-linked hydroxyethylcellulose and any mixture of two or more thereof.

6. A fluid according to any of claims 1 to 5, which further comprises a hydratable polymer solids suspending agent selected from xanthan, succinoglycon, cellulose derivatives, guar, guar derivatives, and any mixtures of two or more thereof.

7. A method of removing filter cake from the walls of a well bore penetrating a producing formation deposited therein by a drilling or servicing fluid as claimed in any of claims 1 to 6, which comprises contacting said filter cake with said clean-up solution for a period of time such that said bridging agent is dissolved thereby.

8. A method of drilling or servicing a well wherein there is used a fluid as claimed in any of claims 1 to 6, and wherein the filter cake formed on the walls of the well bore is removed by treatment with said aqueous clean-up solution.

9. A method according to claim 7 or 8, wherein said clean-up solution contains an organic acid selected from acetic acid, citric acid, adipic acid and glutaric acid, and/or a hydrolyzable ester selected from triethyl citrate, dimethyl glutarate, dimethyl succinate and dimethyl adipate.

10. A method according to claim 7 or 8, wherein said clean-up solution contains an ammonium salt of the formula

$$R_n NH_{4-n}X$$

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EUROPEAN SEARCH REPORT

Application Number
EP 02 25 0108

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
E	EP 1 178 099 A (HALLIBURTON ENERGY SERV INC) 6 February 2002 (2002-02-06) * page 2, line 3 - page 4, line 27 *	1-8,10, 11	C09K7/02 E21B37/06
Y	EP 0 672 740 A (TEXAS UNITED CHEMICAL CORP) 20 September 1995 (1995-09-20)	1-9	
A	* page 3, line 7 - page 6, line 47 *	10,11	
Y,P	WO 01 61148 A (SOFITECH NV, SCHLUMBERGER CA) 23 August 2001 (2001-08-23) * page 3, line 12 - page 4, line 16 * * page 5, line 20 - page 6, line 11 * * page 7, line 17 - page 8, line 30 *	1-9,11	
Y,P	WO 01 83639 A (SCHLUMBERGER HOLDINGS;SOFITECH NV ; SCHLUMBERGER CA LTD (CA); SCHL) 8 November 2001 (2001-11-08) * page 5, line 23 - page 6, line 2 * * page 6, line 20 - line 27 * * page 7, line 15 - page 8, line 6 *	1,7-9,11	

TECHNICAL FIELDS SEARCHED (Int.Cl.7)

C09K
E21B

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	27 May 2002	Boulon, A

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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